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Self-Consistent Effective Binary Diffusion in Multicomponent Gas Mixtures*

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Abstract

The correct treatment of diffusion in multicomponent gas mixtures requires solution of a linear system of equations for the diffusive mass fluxes relative to the mass-averaged velocity of the mixture. Effective binary diffusion approximations are often used to avoid solving this system. These approximations are generally internally inconsistent in the sense that the approximate diffusion fluxes do not properly sum to zero. The origin of this inconsistency is identified, and a general procedure for removing it is presented. This procedure applies equally to concentration, forced, pressure, and thermal diffusion, either separately or in combination. It is used to obtain a self-consistent effective binary diffusion approximation in which the diffusive mass fluxes properly sum to zero and all four types of diffusion are simultaneously accounted for.

Multicomponent diffusion in gases

Multicomponent diffusion in gases is governed by the equations [1]

$$\sum_j (x_i x_j / D_{ij})(\boldsymbol{u}_j - \boldsymbol{u}_i) = \boldsymbol{G}_i \quad (i = 1, \ldots, N), \tag{1}$$

where N is the number of species or components in the mixture, $\boldsymbol{u}_i$ is the specific velocity of species i, x_i is the mole fraction of species i, D_{ij} is the binary diffusivity for the pair (i, j), and the driving forces $\boldsymbol{G}_i$ are given by

$$\boldsymbol{G}_i = \nabla x_i + (x_i - y_i) \nabla \ln p + K_i \nabla \ln T - (1/p)\left[\varrho_i \boldsymbol{F}_i - y_i \sum_j \varrho_j \boldsymbol{F}_j\right]. \tag{2}$$

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Here ϱ_i is the partial mass density of species i, ϱ is the total mass density (i.e., the sum of the ϱ_i), $y_i = \varrho_i/\varrho$ is the mass fraction of species i, p is the pressure, T is the temperature, and $\boldsymbol{F}_i$ is the body force per unit mass acting on species i. The coefficients K_i are simply related to the species thermal diffusion coefficients [1], and they have the property that their sum over all species vanishes.

The diffusive mass fluxes relative to the mass averaged fluid velocity $\boldsymbol{u}$ are given in terms of the $\boldsymbol{u}_i$ by

$$\boldsymbol{J}_i = \varrho_i(\boldsymbol{u}_i - \boldsymbol{u}). \tag{3}$$

These fluxes are needed for closure of the governing equations of motion for a multicomponent fluid, where they appear in the species continuity equations and the energy equation [2, 3].

Equations (1) are N equations in the N unknowns $\boldsymbol{u}_i$. However, only $N-1$ of these equations are linearly independent, as their sum over i yields $\boldsymbol{0} = \boldsymbol{0}$. Equations (1) therefore do not determine a unique solution for the $\boldsymbol{u}_i$. The lack of uniqueness is due to the fact that equations (1) involve only velocity differences, and hence contain no information about absolute velocities. The latter information is contained in the defining equation for the mass-averaged fluid velocity $\boldsymbol{u}$, namely

$$\varrho\boldsymbol{u} = \sum_i \varrho_i\boldsymbol{u}_i. \tag{4}$$

The velocity $\boldsymbol{u}$ is determined by the momentum equation for the mixture [2, 3], and it may therefore be regarded as known. Equation (4) must be taken together with equations (1) to determine a unique solution for the $\boldsymbol{u}_i$ and thereby the $\boldsymbol{J}_i$. It follows from equations (3) and (4) that the diffusion fluxes identically sum to zero,

$$\sum_i \boldsymbol{J}_i = \boldsymbol{0}. \tag{5}$$

Equations (1) and (4) therefore constitute a simultaneous linear system of equations for the velocities $\boldsymbol{u}_i$. The diffusion fluxes are implicitly determined by the solution of this system, which of course entails a certain amount of coding and computational labor. In some cases this is inconvenient, inpractical, or prohibitive. (For example, the diffusion fluxes are often required at many different points in space and time.) It is therefore of interest to develop simple approximations in which the diffusion fluxes are explicitly expressed in terms of the driving forces $\boldsymbol{G}_i$. Effective binary diffusion approximations [2, 4, 5] have been widely used for this purpose. These approximations are based on the idea of approximating $\boldsymbol{J}_i$ by regarding the multicomponent mixture as a binary mixture of species i and a composite species representing all the other species. In this way $\boldsymbol{J}_i$ may be obtained from the simple expressions appropriate to a binary mixture [2]. In the absence of thermal, forced, and pressure diffusion, the most common approximation of this type is [5–7]

$$J_i = -\varrho D_i \nabla(\varrho_i/\varrho), \tag{6}$$

although other forms are also sometimes encountered. The diffusivity D_i in this and similar expressions is an effective binary diffusivity for the diffusion of species i into the rest of the mixture. Various approximations for these effective diffusivities are available [2, 4]. Equation (6) is exact for binary mixtures, with $D_1 = D_2 = D_{12}$. (In fact, it is also exact for multicomponent mixtures when all the D_{ij} are equal [5].)

Effective binary diffusion approximations generally do not satisfy equation (5) unless all the D_i are equal [5]. In most cases this is an unrealistic assumption. In particular, light (low molecular weight) species usually diffuse faster than heavier ones and therefore have larger values of D_i. Thus the D_i will ordinarily be different for different species, and the resulting effective binary diffusion fluxes will violate equation (5). This inconsistency is sometimes simply ignored, but there is no justification for doing so. The most common remedy [5], is to use the effective binary diffusion approximation only for $N-1$ of the fluxes, and then obtain the last one from equation (5). This requires that one of the species be singled out and treated differently from the others, an asymmetry for which there is frequently no physical basis. Our purpose here is to propose a more satisfactory procedure for resolving and removing the inconsistency. The new procedure properly reflects the physical content of equation (1), and it is fully symmetric in all species.

The key to resolving the inconsistency is to inquire how it originates. Diffusion fluxes inconsistent with equation (5) imply specific velocities inconsistent with equation (4), so equation (4) was not properly utilized in the approximation that produced them. The approximation must therefore have been based, either explicitly or implicitly, on equations (1) alone. (Such an approximation, leading to a slight generalization of the usual expression [2, 4, 5] for the D_i, will be presented below.) But we have seen that equations (1) alone are linearly dependent and consequently determine only velocity differences, not absolute velocities. In order for approximate equations (1) to predict absolute specific velocities, the approximation must have had the effect of removing the linear dependence. (That is to say, the singular coefficient matrix corresponding to equations (1) has effectively been approximated by a nonsingular one.) This does not imply that the velocity *differences* have been poorly approximated, but it *does* imply that no significance should be attributed to the velocities themeselves. This is merely a special case of the obvious observation that no approximation, however accurate, can supply information that is not contained in the original problem. Any such additional information is purely an artifact of the approximation, and clearly should not be utilized.

It follows that effective binary diffusion approximations inconsistent with (4) or (5) should only be used to determine differences between the $\boldsymbol{u}_i$ and not their absolute values. But this is tantamount to saying that such approximations determine $\boldsymbol{u}_i$ only to within an unknown additive constant vector $\boldsymbol{C}$. Such a vector should therefore be added to the approximate $\boldsymbol{u}_i$ in much the same way as an undetermined constant of integration is added to an indefinite integral. The unknown vector $\boldsymbol{C}$ can then be determined by requiring equation (4) or (5) to be satisfied, and the overall procedure becomes entirely consistent.

The procedure is therefore as follows. Let velocities and diffusion fluxes predicted by some basic (inconsistent) effective binary diffusion approximation be denoted by a superscript zero. These are uncorrected values which will in general violate equations (4) and (5). According to the preceding discussion, the corresponding consistent approximation to the velocities is

$$\boldsymbol{u}_i = \boldsymbol{u}_i^0 + \boldsymbol{C}, \tag{7}$$

where the vector $\boldsymbol{C}$ must be determined in such a way that (4) is satisfied. Combining (4) and (7) and solving for $\boldsymbol{C}$, we obtain

$$\boldsymbol{C} = \boldsymbol{u} - \sum_i (\varrho_i/\varrho)\boldsymbol{u}_i^0 . \tag{8}$$

The consistent approximation to the velocities then becomes

$$\boldsymbol{u}_i = \boldsymbol{u} + \boldsymbol{u}_i^0 - \sum_j (\varrho_j/\varrho)\boldsymbol{u}_j^0 . \tag{9}$$

The corresponding consistent approximation to the fluxes, obtained by substituting equation (9) into (3), is

$$\boldsymbol{J}_i = \varrho_i \boldsymbol{u}_i^0 - (\varrho_i/\varrho)\sum_j \varrho_j \boldsymbol{u}_j^0 . \tag{10}$$

In terms of the uncorrected (inconsistent) fluxes defined by

$$\boldsymbol{J}_i^0 = \varrho_i(\boldsymbol{u}_i^0 - \boldsymbol{u}),$$

(10) becomes

$$\boldsymbol{J}_i = \boldsymbol{J}_i^0 - (\varrho_i/\varrho)\sum_j \boldsymbol{J}_j^0 . \tag{11}$$

The preceding considerations apply regardless of how equation (1) is approximated to yield approximate species velocities and diffusion fluxes. We now proceed to apply the procedure to a particular approximation to equation (1). We will thereby obtain a self-consistent effective binary diffusion approximation in which the diffusional mass fluxes properly sum to zero and all four types of diffusion are simultaneously accounted for.

As previously remarked, effective binary diffusion is based on the idea of approximating the diffusion of species i as binary diffusion into a complementary composite species representing all the other components. In accordance with this idea, we shall replace the specific velocities of all species other than i in equation (1) by an appropriate mean or effective velocity $\boldsymbol{a}_i$ for the composite species. With this replacement, $\boldsymbol{u}_i$ in equation (1) assumes its effective binary approximate value $\boldsymbol{u}_i^0$. We thereby obtain

$$\boldsymbol{u}_i^0 = \boldsymbol{a}_i - \Big(\sum_{j \neq i} x_i x_j / D_{ij}\Big)^{-1} \boldsymbol{G}_i . \tag{12}$$

We further impose the reasonable consistency requirement that an appropriate weighted average of $\boldsymbol{u}_i^0$ and $\boldsymbol{a}_i$ be independent of which species i has been singled out; i.e.,

$$w_i \boldsymbol{u}_i^0 + (w - w_i) \boldsymbol{a}_i = w \boldsymbol{a} , \tag{13}$$

where the weighted average velocity $\boldsymbol{a}$ is independent of i, w_i are the weighting factors used to define the average, and w is their sum over i. For example, if $w_i = x_i$ then $\boldsymbol{a}$ is a molar average velocity [2].

Equations (12) and (13) vombine to yield

$$\boldsymbol{u}_i^0 = \boldsymbol{a} - (D_i / x_i) \boldsymbol{G}_i , \tag{14}$$

where the effective binary diffusivities D_i are given by

$$D_i = (1 - w_i / w) \Big(\sum_{j \neq i} x_j / D_{ij}\Big)^{-1} . \tag{15}$$

For the natural choice $w_i = x_i$, (15) reduces to the expression usually employed in other treatments [2, 4, 5]. Combining (10) and (14), we obtain

$$\boldsymbol{J}_i = - c M_i D_i \boldsymbol{G}_i + (\varrho_i c / \varrho) \sum_j M_j D_j \boldsymbol{G}_j , \tag{16}$$

where M_i is the molecular weight of species i and c is the total molar concentration of the mixture; i.e., the sum over species of ϱ_i / M_i. Notice that $\boldsymbol{a}$ has dropped out. Equation (16) is our final self-consistent effective binary diffusion approximation. It expresses the diffusive mass fluxes explicitly in terms of the $\boldsymbol{G}_i$, and it manifestly satisfies the constraint of equation (5).

When pressure, forced, and thermal diffusion are neglected, $\boldsymbol{G}_i$ reduces to ∇x_i, and (16) then reduces to the self-consistent binary diffusion approximation used in the APACHE code [4]. That approximation, however, was not based on the present point of view, but was obtained by an entirely different (and somewhat confused) argument [4], in which a clear distinction was not consistently maintained between the exact and approximate diffusion fluxes.

Finally, we observe that since the $\boldsymbol{G}_i$ sum to zero, it follows from (14) that

$$\boldsymbol{a} = \Big(\sum_i x_i/D_i\Big)^{-1} \sum_i (x_i/D_i)\boldsymbol{u}_i^0 . \tag{17}$$

Equation (17) shows that $\boldsymbol{a}$ may be regarded as a weighted average of the $\boldsymbol{u}_i^0$, but with weighting factors that differ in general from the w_i. This in turn suggests that a natural preferred choice for the w_i is to define them in such a way that $w_i = x_i/D_i$. With this choice, equations (13) and (17) combine to imply that $\boldsymbol{a}_i$ is just the w_i-weighted average of the $\boldsymbol{u}_i^0$ with $j \neq i$, which intuitively seems a desirable additional consistency property. Unfortunately, it is inconvenient to choose the w_i in this way, because D_i itself is proportional to $(1 - w_i/w)$. The condition $w_i = x_i/D_i$ is therefore quadratic in w_i for a given w, and the constraint that the w_i must sum to w is too complicated to analytically enforce. This choice for the w_i is therefore unlikely to be useful, as it does not lead to simple explicit expressions for the D_i.

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